

PATENT ABSTRACTS OF JAPAN

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(54) POLYESTER RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyester composition having an improved hydrolytic resistance (thermal aging resistance) and stretch characteristics without causing an large increase in the melt viscosity.

SOLUTION: The polyester resin composition is obtained by kneading 90-99.9 wt.% of a thermoplastic polyester resin and 0.1-10 wt.% of a liquid polybutene having an epoxy group at its terminal in a molten state to introduce a polybutylene chain into the polyester simultaneously with blocking the terminal carboxy group of the polyester.

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CLAIMS

[Claim(s)]

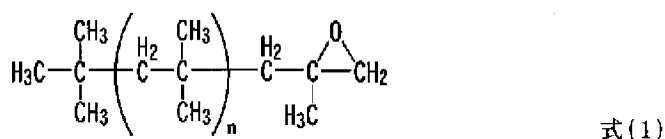
[Claim 1]

A polyester resin composition produced by carrying out melt kneading of 0.1 to 10 % of the weight (both are made into 100 % of the weight in all.) of the liquefied polybutene which has an epoxy group at 90 to 99.9 % of the weight of thermoplastic polyester, and the end.

[Claim 2]

The polyester resin composition according to claim 1, wherein more than 80 mol % in liquefied polybutene which has an epoxy group at the end is what has the structure of a formula (1).

[Formula 1]



(式中nは、1～180の整数である。)

[Claim 3]

A polyester system resin composition given in either claim 1, wherein liquefied polybutene which has an epoxy group at the end is obtained from liquefied polybutene of the number average molecular weights 200-10,000, or claim 2.

[Claim 4]

A polyester system resin composition given in either claim 1, wherein liquefied polybutene which has an epoxy group at the end is obtained from liquefied polybutene of the number average molecular weights 250-3,500, or claim 2.

[Claim 5]

A polyester resin Plastic solid which is a Plastic solid acquired from the polyester system resin composition according to any one of claims 1 to 4, and is characterized by passing through a stretching process.

[Claim 6]

A monofilament obtained from the polyester resin composition according to any one of claims 1 to 4.

[Claim 7]

Industrial use textiles, wherein the woof and/or warp use at least a monofilament obtained from the polyester resin composition according to any one of claims 1 to 4 in part.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to a polyester resin composition suitable for shaping which needs the intensity grant by the stretching process of the polyester resin composition in which hydrolysis resistance (heat-resistant aging nature) and melt viscosity stability were improved especially a monofilament, textiles, a sheet, a film, a hollow container, etc.

[0002]

[Description of the Prior Art]

The polyester resin which makes polyethylene terephthalate representation, After adding the inorganic filler aiming at rigidity and heat-resistant improvement if needed as mold goods to which intensity was added by the stretching process of a monofilament, textiles, a film, a hollow container, etc., it is used by injection molding as mold goods of arbitrary shape. Although polyester resin products have mechanical properties excellent in the general target, the characteristic falls by hydrolysis and there is a fault of hue also getting worse under an elevated temperature and humid environment.

[0003]

The textiles in which, especially as for the tendency, the woof and/or warp used polyesters monofilaments and polyesters monofilaments in part at least, For example, it was remarkable in industrial use textiles, such as ** for paper-making dryer canvas, a paper-making wire, a filter, a conveyor belt, and screens.

[0004]

Existence of the terminal carboxyl group in a polyester molecule is pointed out as a factor which promotes this hydrolysis, and the art of carrying out chemical modification of the carboxyl group concerned, and raising hydrolysis resistance is proposed.

[0005]

The improved method of typical hydrolysis resistance is a method of making a terminal carboxyl group reacting to a carbodiimide system compound or a poly carbodiimide compound. For example, the art of making a chain constructing a bridge and raising a molecular weight is indicated by JP,10-168655,A and JP,10-168661,A at the same time a poly carbodiimide compound blocks the terminal carboxyl group of polyester. However, there is a problem of toxicity, a price, and hue in a carbodiimide system compound. As other methods, the method of making a terminal carboxyl group react to an epoxy group containing compound is indicated. However, the publicly known method of using an epoxy group containing compound has a problem about the influence on the earliness of a reaction, and the other characteristics.

[0006]

Although refining by 1 which has a polyester type block copolymer and polyether structure, and 2 organic-functions epoxy compound is indicated in JP,3-77826,B, The melting characteristic becomes very unstable, when a heat-resistant problem is among the constituents obtained and the amount ingredient of polymers arises with the epoxy compound of two or more organic functions.

[0007]

In JP,10-245475,A, refining by the reaction of a polyester elastomer and various epoxy denaturation polymer is indicated. However, the thing illustrated as epoxy denaturation polymer, The polymer which has a carbon carbon double bond, and these partially-hydrogenated polymer Hydrogen peroxide, The polymer epoxidated by processing with peracetic acid or other peroxy acids, Using a radical initiator or an activity energy line, to polymer backbone, although it is graft denaturation or the polymer which carried out copolymerization, the polymer which carried out copolymerization to glycidyl (meta) KURIRETO, ethylene, styrene, etc., and the above-mentioned glycidyl (meta) KURIRETO monomer, There are problems, like if these are used, the melt viscosity of a constituent will increase substantially, or the heat deterioration and oxidation degradation of the carbon carbon double bond portion in the polymer for refining which remains

arise.

[0008]

As a thing about the industrial use textiles using polyesters monofilaments excellent in hydrolysis resistance, and its polyesters monofilaments, although there is the patent No. 3247790, Manufacture of the diepoxy compound which makes a subject the para-hydroxybenzoic acid diglycidyl ester ether to be used is not [making the carbodiimide compound indispensable,] easy, This epoxy compound is straight chain structure which has an ether bond, and since the improvement effect of melt tension being small and an amorphous structure part do not exist substantially, the hot welding characteristic of the woof and warp in industrial use textiles has problems, such as taking.

[0009]

[Problem(s) to be Solved by the Invention]

A material suitable for refining which this invention can raise the efficiency which participates in polyester directly in view of an above-mentioned situation, and can reveal modification effect with an addition sufficient also in a small quantity is provided, And the constituent obtained, maintaining various characteristics, such as heat resistance, the transparency, etc. of a polyester main part. The suitable increase in melt viscosity and melt tension is made, and it aims at providing a polyester resin composition, polyesters monofilaments, and industrial use textiles excellent in the intensity addition nature and hot welding nature to a product by extension.

[0010]

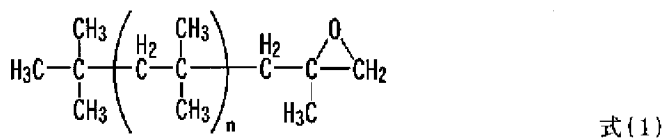
[Means for Solving the Problem]

It is related with a polyester resin composition produced by carrying out melt kneading of the mixture containing 0.1 to 10 % of the weight (both are made into 100 % of the weight in all.) of liquefied polybutene which has an epoxy group at 90 to 99.9 % of the weight of the 1st polyester of this invention, and the end.

[0011]

It is related with a polyester resin composition being that in which more than 80 mol % in liquefied polybutene which has an epoxy group at the end has the structure of formula (I) in the 1st [of this invention] of the 2nd this invention.

[Formula 2]



(式中nは、1～180の整数である。)

[0012]

It is related with a polyester system resin composition in which liquefied polybutene which has an epoxy group at the end in the 1st [of this invention] of the 3rd this invention or the 2nd is characterized by being obtained from liquefied polybutene of the number average molecular weights 200-10,000.

[0013]

It is related with a polyester system resin composition in which liquefied polybutene which has an epoxy group at the end in the 1st [of this invention] of the 4th this invention or the 2nd is characterized by being obtained from liquefied polybutene of the number average molecular weights 250-3,500.

[0014]

It is related with a polyester resin Plastic solid passing through a stretching process which is a Plastic solid acquired from a polyester system resin composition of the 1-4th either of the 5th this invention of this invention.

[0015]

It is related with a monofilament obtained from a polyester resin composition of the 1-4th either of the 6th this invention of this invention.

[0016]

It is related with industrial use textiles, wherein the woof and/or warp use at least a monofilament obtained from a polyester resin composition of the 1-4th either of the 7th this invention of this invention in part.

[0017]

[Embodiment of the Invention]

If polyester concerning <polyester> this invention is thermoplastic polyester, there will be no restriction in particular, but. Preferably Polyethylene terephthalate (PET), polybutylene terephthalate (PBT), Polyethylenenaphthalate (PEN), Poly 1, 4-cyclohexane dimethylene terephthalate (PCT), The thermoplastic polyester elastomer, half-aromatic liquid crystal polyester, and all the aromatic liquid crystal polyester which make these a hard segment and use polyether, amorphous polyester, etc. as a soft segment are included. That an effect is most acquired in these are crystalline polyester (PET, PBT, PCT, etc.) which makes terephthalic acid and diol the main repeating unit. Especially a desirable thing from a viewpoint to avoid that melt kneading temperature becomes an elevated temperature too much. It is a thermoplastic polyester elastomer which makes PET and PBT, and these a hard segment, and uses polyether, amorphous polyester, etc. as a soft segment, and since the manifestation of an orientation effect is large, PET is preferred.

[0018]

The liquefied polybutene (henceforth "epoxy group content liquefied polybutene") which has an epoxy group at the end of a <epoxy group content liquefied polybutene> chain can epoxidate and obtain end carbon and the carbon double bond in the chain of liquefied polybutene by a publicly known method. C4 fraction [in / in the liquefied polybutene of a raw material / oil refining] from FCC, By disassembly of naphtha and other hydrocarbon, are C4 fraction etc. to produce and Isobutylene, Butene-1, the thing containing butane other than the butene- 2, or the thing which added isobutylene etc. to C4 fraction and adjusted the presentation to it is polymerized and obtained by Friedel-Crafts catalysts, such as an aluminium chloride and boron trifluoride, etc. The main constitutional unit of liquefied polybutene originates in isobutylene. Although a carbon carbon double bond exists in the end piece of liquefied polybutene and the structure has a vinyl type, a vinylidene type, etc., for the purpose of this invention, a vinylidene type is preferred. The manufacturing method of the liquefied polybutene which has such an end vinylidene group is indicated to JP,10-306128,A etc.

[0019]

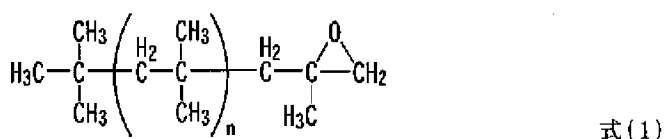
Epoxy group content liquefied polybutene can be obtained by a publicly known method. For example, the method of peracetic acid and sodium acetate being dropped and manufacturing epoxy group content liquefied polybutene is shown in JP,51-8966,B, stirring liquefied polybutene and n-hexane. Although the same method is indicated by European patent publication-before-examination EP045749, the U.S. Pat. No. 3,382,255 gazette, etc., these methods can also be used

preferably.

[0020]

In this invention, it is preferred that more than 80 mol % of epoxy group content liquefied polybutene is a lower type (1).

[Formula 3]



(式中nは、1～180の整数である。)

Since the epoxy group content liquefied polybutene of a formula (1) does not have the 3rd class carbon atom substantially, it is excellent in heat-resistant degradation nature and anti-oxidation degradation nature, also at the melting working temperature of polyester, is stable, and excellent also in long-term stability. the structure concerned -- more than 80 mol % -- the molecule in which the included epoxy group content liquefied polybutene has an end vinylidene group -- more than 80 mol % -- if the included liquefied polybutene is used as a raw material, it can obtain easily. Such liquefied polybutene is obtained by polymerizing under existence of a boron trifluoride complex compound catalyst in C4 fraction containing the publicly known method indicated to JP,10-306128,A etc., for example, an isobutylene independent, and butene-1 and butene-2 grade other than isobutylene.

[0021]

In this invention, it is preferred that epoxy group content liquefied polybutene is obtained from liquefied polybutene of the number average molecular weights 200-10,000 (number average molecular weight by GPC measurement (polystyrene reduced property)) within the limits. Melt viscosity improvement of melting polyester is not enough in a number average molecular weight being less than 200, and if 10,000 is exceeded, reactivity at the time of melt kneading will fall.

[0022]

A number average molecular weight of liquefied polybutene makes it still more desirable within the limits of 250-10,000. In within the limits of this, reservation of an effect of intensity addition nature to a product and hot welding nature by extension of polyester becomes easy. When reactivity is also taken into consideration, it carries out within the limits of 250-3,500, and is

within the limits of 250-1,400 still more preferably.

[0023]

When epoxy group content liquefied polybutene obtained from liquefied polybutene of a number average molecular weight of the range concerned combines with polyester system resin via an epoxy group, a polybutene chain connected with the bond part concerned is very short inevitably, if it compares with a polyester chain. Therefore, with this structure, since it is hard to generate phase separation structure (sea island structure), it does not check the transparency of polyester system resin.

[0024]

An epoxy group (oxirane group) of epoxy group content liquefied polybutene concerning this invention is arranged at the end. For this reason, compared with an epoxy group (oxirane group) arranged in usual reactant oligomer or long chain structure of a reactive polymer compound, reactivity with a carboxyl group in polyester and/or a hydroxyl group is very high. Structure of a molecule generated by the reaction of polyester and epoxy group content liquefied polybutene, It has hydrocarbon oligomer or branching which has branching in an end piece of a polyester molecule of a basis, and is rich in flexibility in it compared with a polyester molecule chain, and is rich in flexibility compared with a polyester molecule chain, and becomes the structure which a hydrocarbon high molecular compound which is very easy to produce an intermolecular interaction added. As a result, melt viscosity and melt tension of melting polyester increase. A degree of this increase can be adjusted with the characteristics, such as a molecular weight of polyester, and the end carboxy group equivalent, a molecular weight of epoxy group content liquefied polybutene, and an addition.

[0025]

Epoxy group content liquefied polybutene combined with an end of a polyester molecule chain, Since it functions as a soft segment introduced into polyester resin, stiffness is eased and, as for industrial use textiles in which the woof and/or warp used at least a monofilament obtained from the polyester concerned in part, the hot welding characteristic between monofilaments is improved.

[0026]

In this invention, to 90 to 99.9 % of the weight of polyester system resin in kneaded material, it adds 0.1 to 10% of the weight, and melt kneading of the epoxy group content liquefied polybutene is carried out. If an effect is not fully acquired as it is less than 0.1 % of the weight, but it exceeds 10 % of the weight, unreacted epoxy group content liquefied polybutene will remain in a final composition thing, and will produce problems, such as bleeding. When a number average molecular weight of epoxy group content liquefied polybutene is small, for avoiding that glue stock and a problem to attach arise, 5 or less % of the weight is preferred.

[0027]

Since epoxy group content liquefied polybutene concerning this invention is a fluid, as it is, Or it can apply to the surfaces, such as polyester system resin before a melt kneading start, easily and uniformly by diluting with warming or other solvents if needed, and mixing with polyester system resin etc. with stirring mixers, such as a Henschel mixer and a tumbler mixer. As a result, supply to a kneading machine of the polyester concerned is stable. douche ON by epoxy group content liquefied PORIBU and douche ON with a pump -- being certain -- it may be and may add before melting of polyester, or to the back using natural dropping from a vent-port, etc.

[0028]

In melt kneading, if a catalyst is used, an effect of this invention can be heightened. What is necessary is just to use as a catalyst what is used as a reaction of epoxy generally. For example, it is metal salt of periodic-table-of-the-elements I-a fellows of an amine compound, phosphorus compounds and ten or more monocarboxylic acid or with a number of carbon atoms, and dicarboxylic acid, or II-a fellows. They are especially desirable trivalent phosphorus compounds, such as tributyl phosphine triphenylphosphines. These may use two or more kinds together.

[0029]

In melt kneading temperature of polyester epoxy group content liquefied polybutene, Since it has volatility sufficient in the bottom of atmospheric pressure or decompression, among a melt kneading process of a kneading machine preferably, When decompression sucking is carried out with a vacuum pump etc. and unreacted epoxy group content liquefied polybutene remains preferably by providing a clear aperture in a final process, these can in part or all be removed out of a system, and it is effective in characteristic stabilization of a final product.

[0030]

as for thermoplastic polyester system resin and epoxy group content liquefied polybutene, more than the melting point of this polyester is desirable temperature higher 5-100 °C than the melting point, especially a desirable temperature high 10-60 °C, and it reacts easily by coming out and carrying out melt kneading. A reaction mentioned above should just select conditions fully performed, a thing for 20 seconds - 10 minutes to do for between melt kneading is desirable still more preferred, and kneading processing time is 40 seconds - 3 minutes especially preferably for 30 seconds - 5 minutes. If kneading temperature and time are less than these ranges, and a reaction will not fully advance but will exceed, decomposition and an anomalous reaction of thermoplastic polyester system resin are produced, and it is not desirable.

[0031]

There is no restriction in apparatus which carries out melt kneading in any way, and publicly known apparatus, such as a Banbury mixer, a roll, a monopodium extruding kneading machine, and a biaxial extruding kneading machine, can be used for melt kneading apparatus and a concrete target equipped with heating equipment. These apparatus did not necessarily need to be formed into apparatus which manufactures a pellet, and mono- ***** could be provided into a multifilament manufacturing machine, a container manufacturing machine, a sheet manufacturing machine, and arbitrary making machines of an injection molding machine this. a desirable method of acquiring an effect of this invention is a method of supplying one axis or a biaxial extrusion machine, carrying out melt kneading treatment 1 minute or more preferably 30 seconds or more, and manufacturing a pellet, after mixing a predetermined ingredient uniformly with a tumbler or a mixer like a Henschel mixer.

[0032]

A polyester resin composition of this invention An inorganic filler, for example, calcium carbonate, Titanium oxide, a feldspar system mineral, clay, white carbon, carbon black, At the time, such as a glass bead, a granular or formless bulking agent, kaolin clay, A fibrous bulking agent can be added at the time, such as scale-like bulking agent; glass fiber, carbon fiber, wollastonite, and potassium titanate, at the time, such as a time [, such as talc,] tabular bulking agent, a glass flake, mica, and graphite. Additive agents, such as other polymer, an antioxidant, a thermostabilizer, an ultraviolet ray absorbent, lubricant, a nucleating additive, a plasticizer, a release agent, paints, and a shock improving agent like various elastomers, may be added further if needed. Therefore, what was produced by blending and carrying out melt kneading of liquefied

polybutene which has an epoxy group at thermoplastic polyester and the end, and the ingredients other than these to a polyester resin composition in this invention is included.

[0033]

[Example]

Hereafter, although this invention is further explained in full detail according to an example, this invention is not limited with this.

Trade name LV-50 (Mn=430, the Nippon Oil chemicals incorporated company make) is used as <manufacture of epoxy group content liquefied polybutene> (example 1 of manufacture) liquefied polybutene, The mixture of peracetic acid (40-% of the weight acetic acid solution) and sodium acetate is dropped putting in and stirring liquefied polybutene and n-hexane in a cooling system, heating apparatus, and a reaction vessel with a dephlegmator at JP,51-8966,B according to the method of a statement. Perform regulation of dropping speed and cooling, make it react at 20-30 **, and it stirs after the end of dropping, Subsequently, n-hexane was removed by distillation under reduced pressure, output was poured out underwater, evaporative removal of the ether was carried out through washing by ether extraction, water, and sodium carbonate, and desiccation, and the mixture which contains the liquefied polybutene (it has the structure of the formula 1 and is n= 4-8) which has an epoxy group at the end 15% of the weight was obtained. Hereafter, this is called "epoxy group content liquefied polybutene A."

(Example 2 of manufacture) the end vinylidene structure acquired by the manufacturing method of JP,10-306128,A -- 85-mol % -- the mixture which contains the liquefied polybutene which has an epoxy group at the end like the above-mentioned example 1 of manufacture 70% of the weight was manufactured using the polybutene (Mn=250) to contain. Hereafter, this is called "epoxy group content liquefied polybutene B."

(Example 3 of manufacture) the end vinylidene structure acquired by the manufacturing method of JP,10-306128,A -- 85-mol % -- using the polybutene (Mn=800) to contain, The mixture which contains the liquefied polybutene (it has the structure of the formula 1 and is n= 10-14) which has an epoxy group at the end like the above-mentioned example 1 of manufacture 70% of the weight was manufactured. Hereafter, this is called "epoxy group content liquefied polybutene C."

[0034]

After drying the polyethylene terephthalate chip of <comparison of hydrolysis resistance (heat-resistant aging nature) under hot environments> (example 1) intrinsic viscosity 0.9, it put into the drum tumbler, and five weight sections of "epoxy group content liquefied polybutene A" was

added, and it mixed. It continued, and supplied to the hopper of the biaxial melt kneading machine of screw diameter [of 46 mm] phi (ratio-of-length-to-diameter=36), melt kneading was carried out by barrel maximum-temperature 280 **, and it pelletized at the process extruded, water-cooled and omitted from a dice. The open vent-port was provided near the dice, the vacuum pump was operated, and volatile matter content was removed. It was 40 seconds when the injection pellet measured the time which is conveyed by the screw from under a hopper and is extruded from a dice with the color pellet. Most discoloration was not observed, although it continued, this pellet was put into the petri dish and it was neglected in 140 ** gear oven for 24 hours.

[0035]

(Example 2)

After drying the polyethylene terephthalate chip of intrinsic viscosity 0.9, it put into the drum tumbler, and the amount part addition of duplex of "the epoxy group content liquefied polybutene B" was carried out, and it mixed. It continued, and supplied to the hopper of the biaxial melt kneading machine of screw diameter [of 46 mm] phi (ratio-of-length-to-diameter=36), melt kneading was carried out by barrel maximum-temperature 280 **, and it pelletized at the process extruded, water-cooled and omitted from a dice. The open vent-port was provided near the dice, the vacuum pump was operated, and volatile matter content was removed. It was 40 seconds when the injection pellet measured the time which is conveyed by the screw from under a hopper and is extruded from a dice with the color pellet. Discoloration was not observed, although it continued, this pellet was put into the petri dish and it was neglected in 140 ** gear oven for 24 hours.

[0036]

(Example 3)

After drying the polyethylene terephthalate chip of intrinsic viscosity 0.9, it put into the drum tumbler, and four weight sections of "epoxy group content liquefied polybutene C" was added, and it mixed. It continued, and supplied to the hopper of the biaxial melt kneading machine of screw diameter [of 46 mm] phi (ratio-of-length-to-diameter=36), melt kneading was carried out by barrel maximum-temperature 280 **, and it pelletized at the process extruded, water-cooled and omitted from a dice. The open vent-port was provided near the dice, the vacuum pump was operated, and volatile matter content was removed. It was 60 seconds when the injection pellet measured the time which is conveyed by the screw from under a hopper and is extruded from a

dice with the color pellet. Discoloration was not observed, although it continued, this pellet was put into the petri dish and it was neglected in 140 °C gear oven for 24 hours.

[0037]

(Comparative example 1)

The polyethylene terephthalate chip of intrinsic viscosity 0.9 was dried. It continued, and supplied to the hopper of the biaxial melt kneading machine of screw diameter [of 46 mm] phi (ratio-of-length-to-diameter=36), melt kneading was carried out by barrel maximum-temperature 280 °C, and it pelletized at the process extruded, water-cooled and omitted from a dice. The open vent-port was provided near the dice, the vacuum pump was operated, and volatile matter content was removed. It was 60 seconds when the injection pellet measured the time which is conveyed by the screw from under a hopper and is extruded from a dice with the color pellet. It continued, and yellowing was observed, when this pellet was put into the petri dish and it was neglected in 140 °C gear oven for 24 hours.

[0038]

The motor load when the amount of extrusion was made the same per [which starts the amount of extrusion and kneading in the comparative example 1 per / concerning kneading in the <comparison of extension performance> example 3 / unit time] unit time was measured, and it checked that the melt viscosity rise in which each load is almost the same and steep had not arisen. It continued and the maximum winding rotation speed which is made to increase the revolving speed of the strand winding roll of a pelletizer, and a strand piece does not produce was found on each condition. It of Example 3 was 120% of the comparative examples 1.

[0039]

It turned out that it is the material which fitted the mold goods which need intensity grant according to hydrolysis-proof and a stretching process especially by not accompanying the polyester resin composition applied to this invention from the above result by steep melt viscosity rise, but improving hydrolysis resistance (heat-resistant aging nature) and the extension characteristic.

[0040]

[Effect of the Invention]

In this invention, the hydrolysis resistance of thermoplastic polyester system resin can be improved for good productivity, without changing the melting characteristic substantially, and the extension characteristic is improved.

Therefore, a material suitable for the mold goods which need the intensity grant especially by hydrolysis resistance and a stretching process can be obtained.

[Translation done.]